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Methyl bonding to Fe and Fe(CO)$_n$: reactions of Fe$^-$ and Fe(CO)$_n^-$ with methyl halides

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Abstract

Rate constants for atomic iron anion and successively ligated anions Fe(CO)$_n^-$ ($n = 0$–4) reacting with CH$_3$X (X = F, Cl, Br, I) were measured using a selected-ion flow tube apparatus. The results indicate that X$^-$ formation occurs as the dominant channel when exothermic. Other observed reaction channels are ligand exchange (with CH$_3$ and X replacing two CO), halogen-atom abstraction and adduct formation. Fe(CO)$_4^-$ is too stable for a reaction with CH$_3$X to develop by any channel. Fe(CO)$_2^-$ displays a rich chemistry. Information on the bond strengths, D[Fe(CO)$_n$–CH$_3$], is deduced from the results. Under the assumption that the X$^-$ product channel is observed if exothermic, we calculate the homolytic iron–methyl bond energies $0.13\ \mathrm{eV} \leq D[\mathrm{Fe–CH_3}] \leq 1.76\ \mathrm{eV}$, $D[\mathrm{Fe(CO)–CH_3}] = 1.2 \pm 0.2$ eV, $D[\mathrm{Fe(CO)_2–CH_3}] = 1.3 \pm 0.3$ eV, $D[\mathrm{Fe(CO)_3–CH_3}] < 1.4$ eV, and $D[\mathrm{Fe(CO)_4–CH_3}] < 2.1$ eV. (Int J Mass Spectrom 195/196 (2000) 341–349) © 2000 Elsevier Science B.V.

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1. Introduction

Relatively little is known about reactions of negative ions of transition-metal complexes, compared to their positive ion siblings, though it seems clear that the anions are, generally speaking, less reactive. Research through 1986 has been reviewed by Squires [1], who pointed out the need specifically for data on metal ion complexes with intermediate degrees of coordinative unsaturation, in order to connect the simpler atomic anion chemistry with the better-known chemistry of coordination compounds in condensed phases. Since that time there has been ever-increasing activity in this area of research, and a comprehensive review is not in order here. We summarize the negative ion chemistry of the Fe(CO)$_n^-$ and Fe(CO)$_5$ only.

The negative ion chemistry of Fe(CO)$_5$ has been one of the more well-studied systems, in part because Fe(CO)$_5$ is inexpensive, commercially available, air stable, and quite volatile. Early work by Compton and Stockdale [2] on the electron impact appearance potentials of the various Fe(CO)$_n^-$ fragments led to thermodynamic information on the Fe(CO)$_n^-$. This was easily linked to neutral thermochemistry when the electron affinities (EAs) of the entire Fe(CO)$_n$

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Dedicated to Bob Squires for his seminal contributions to mass spectrometry and ion chemistry.

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series, including Fe, were reported by Engelking and Lineberger [3]. Sunderlin et al. [4] made use of the EA data in their determination of the carbonyl bond energies in $Fe(CO)_n^-$, again linking ion and neutral thermochemistries. Somewhat more accurate EAs are now available for Fe [5], Fe(CO) [6], $Fe(CO)_2$ and $Fe(CO)_3$ [7].

Dunbar et al. [8] in 1973 were apparently the first to make observations of ion–molecule reactions of negative ions of transition-metal carbonyls, including $Fe(CO)_5$. They reacted fragment ions with their parent vapors, noting the formation of dinuclear metal anions. Shortly thereafter, Foster and Beauchamp [9] made similar observations, and in addition reacted a few foreign negative ions with $Fe(CO)_5$. Both groups [8,9] found $Fe(CO)_4^-$ to be nonreactive. McDonald et al. [10] reacted $Fe(CO)_3^-$ with several neutrals; with CH_3Br they found both Br atom transfer and ligand displacement. Pan and Ridge [11] focused on reactions of 17-electron species, including $Fe(CO)_4^-$, with organic molecules that had EAs above and below that of $Fe(CO)_4^-$ and observed loss of 1, 2, and 4 CO ligands.

Jones et al. [12] used a flowing afterglow apparatus to measure reaction rate constants for a large number of reactions of 17-electron transition-metal negative ion complexes with haloalkanes. The products showed halogen atom transfer. Of particular relevance to the present work, Jones et al. [12] found no reaction for $Fe(CO)_4^-$ interacting with CH_3X (X = Cl, Br, I), as also reported earlier by McDonald et al. [13].

A number of other laboratories have reported reactions of various $Fe(CO)_n^-$ with neutrals, including reactions of $Fe(CO)_3^-$ and $Fe(CO)_4^-$ with *n*-chloroalkanes, *n*-alcohols, 1,*n*-bromochloroalkanes, 1,*n*-chloroalcohols, nitroalkanes, and *n*-butyl nitrite by McElvany and Allison [14,15]. McDonald and coworkers examined the reactions of $Fe(CO)_2^-$ with $(CH_3)_2O$, CH_4, $(CH_3)_4$ and other alkanes [16,17], H_2, H_2O, H_2S, NH_3, and PH_3 [18]. Recent work includes reactions of $Fe(CO)_2^-$ with hydrocarbons [19], $Fe(CO)_{2-4}^-$ with isotopically labeled CO_2 [20], $Fe(CO)_2^-$ with isotopically labeled alcohols [21], $Fe(CO)_{2,3}^-$ with isotopically labeled OCS, [22], $Fe(CO)_{1-3}^-$ with *n*-heptane, H_2O and CH_3OH [23], $Fe(CO)_2^-$ with isotopically labeled CH_3OH [24], $Fe(CO)_{0-3}^-$ with isotopically labeled methyl formate [25], and $Fe(CO)_{1-4}^-$ with N_2O and O_2 [26].

An interesting reaction was noted by Miller and Beauchamp [27] in which $Fe(CO)_4^-$ reacts with the parent $(CO)_4FeH_2$,

$$Fe(CO)_4^- + (CO)_4FeH_2 \rightarrow (CO)_4FeH^- + (CO)_4FeH \quad (1)$$

This apparent proton transfer reaction shows the acidity of $(CO)_4FeH$ is less than that of $(CO)_4FeH_2$, which when coupled with the EA[$Fe(CO)_4$] places a lower limit on the bond energy $D[(CO)_4Fe–H] \geq 2.60 \pm 0.52$ eV.

In a collaboration between the Squires and Freiser groups at Purdue University, Sallans et al. [28,29] developed a method for studying reactions of atomic anions of transition metals using collision-induced dissociation with a Fourier transform ion cyclotron resonance apparatus. They found the atomic metal anions—unlike the cations—to be completely unreactive with saturated and unsaturated hydrocarbons. This difference in reactivity was attributed to the doubly occupied *s* orbitals of the anions, which have configurations d^ns^2, as compared to the d^n or $d^{n-1}s^1$ configurations of the cations. However, proton transfer reactions with relatively strong acids were observed by Sallans et al. [29]. Later, Sallans et al. [30] found that atomic transition-metal anions tend to react with organic sulfur-containing compounds, with a preference for cleaving the C–S bond and retention of the negative charge by the metal-bearing product. Lane, et al. [31] reacted a large variety of negative ions (X^-) with $Fe(CO)_5$, observing products of the type $(CO)_4Fe(CO)X^-$, $(CO)_4FeX^-$, and $(CO)_3FeX^-$.

Reactions of bare Fe^- and $Fe(CO)_n^-$ with various molecules have been studied in this laboratory. In one work, Fe^- reactions were used to bracket the gas-phase acidity of FeH, which yields the bond energy $D[Fe–H] = 1.52 \pm 0.19$ eV [32]. In another work, we reacted the full range successively carbonylated species, from Fe^- through $Fe(CO)_4^-$ with a neutral, SF_4 [33]. We have also reacted $Fe(CO)_n^-$ with trifluoromethyl halides [34]. A propensity for formation of iron fluorides (both as neutrals and as anions) in reactions with fluorinated neutrals has been noted [32–34].

The present study exploits our ability to readily produce the full range of the anions, from Fe^- through $Fe(CO)_4^-$, for study. We have used a selected ion flow tube (SIFT) apparatus to determine rate constants at 297 K for reactions of $Fe(CO)_n^-$ (n = 0–4) with the methyl halides. This work was motivated in part by an interest in the iron–methyl bond energies of the $Fe(CO)_nCH_3$. The comparison between the reaction channels active for Fe^- and for successively ligated $Fe(CO)_n^-$ suggests the reaction pathways are largely driven by energetics, enabling us to estimate the iron–methyl bond energies. In addition to providing fundamental data, the energetics may help to provide insight into the differing reaction paths of the various $Fe(CO)_n^-$ with other neutrals.

2. Experiment

These experiments were carried out at the Air Force Research Laboratory on a SIFT apparatus which has been described earlier [35]. Ions were created in an electron bombardment ion source and were mass selected before injection through a helium aspirator into a flow tube reactor. The throughput of helium buffer gas was 8.8 std. L min^{-1}, the helium bulk flow speed was 14 000 cm s^{-1}, and the average pressure was 0.4 Torr. A small amount of methyl halide vapor (a partial pressure equal to a few ten-thousandths that of the buffer) was introduced through a perforated ring inlet at either of two points along the flow tube. The use of two reaction distances (50.3 and 35.4 cm) allowed compensation for the end correction associated with mixing of the reactant and buffer gases. At the end of the reaction zone, a sample of the ions passed into a high vacuum region for mass analysis and detection. Reaction rate constants were obtained from the exponential attenuation of the primary ion signal by the methyl halide vapor. The reaction time was determined from the reaction distances and ion time-of-flight measurements. The rate constants are considered accurate to ±25%. The gaseous methyl halide reactants were used as supplied. Several freeze–pump–thaw cycles were used to degas CH_3I. Results for the single reaction in which ion products were observed with CH_3F reactant [in reaction with $Fe(CO)_2^-$] included unexplained ion products which we attribute to impurities in the CH_3F (see footnote e in Table 1). In some cases (as noted in the footnotes to Table 1) an electric drift field was applied to increase the ion kinetic energy, but little new information *vis-à-vis* bond strengths was obtained. In the footnotes to Table 1, E_{cm} denotes the center-of-mass energy for the ion–molecule system [35].

With $Fe(CO)_5$ vapor in the ion source, electron bombardment produced primarily $Fe(CO)_4^-$ ions. Barely usable currents of mass analyzed $Fe(CO)_{1-3}^-$ could also be extracted from the source. It proved far more effective to produce these ions by injecting $Fe(CO)_4^-$ into the flow tube at sufficient energy to dissociate it upon collision with helium atoms. The production of $Fe(CO)_3^-$ was optimal at a center-of-mass energy of 1.1 eV; $Fe(CO)_2^-$ at 1.7 eV; $Fe(CO)^-$ at 2.6 eV; and Fe^- at 4.1 eV. The greater intensities of $Fe(CO)_n^-$ (n = 1–3) generated by collision-induced dissociation allowed the reaction rate constants to be measured more accurately. However, the product branching ratios were complicated by having more than one primary ion present in the flow tube. Hence, reaction products were determined by injecting only one particular ion type into the flow tube, in the usual SIFT mode of operation. Conducting deposits due to thermal dissociation of $Fe(CO)_5$ in the ion source led to failure of the source after 2–3 days of operation. The best performance was obtained using a 10% mixture of $Fe(CO)_5$ in argon, and a cooler electron filament (thoriated iridium).

3. Results

Reaction rate constants and ionic products are presented in Table 1. Neutral products were not observed in the present experiment. Energetic constraints generally dictate the neutral product to exist as shown. In some cases the exothermicity is such that additional Fe–ligand bonds may be broken, for exam-

Table 1
Reactions studied in this work, with measured total rate constants k_{exp} (in units of 10^{-9} cm^3 s^{-1}), reaction efficiencies (rxn eff), and product branching fractions (frac); the final column gives the reaction enthalpy (ΔH_{rxn}, in eV) for the channel producing X^-, regardless of whether or not it is observed; the enthalpy is given in terms of the unknown bond energy, $D[Fe(CO)_n–CH_3]$, denoted by D_n; the number in parentheses in the enthalpy column is the uncertainty in the final digit(s) of the energy listed

k_{exp}	rxn eff[a]	Reaction	frac	ΔH_{rxn} (X^- channel)
<0.001	0	$Fe^- + CH_3F \rightarrow$ no reaction		$1.64(12) - D_0$
0.77[b]	0.4	$Fe^- + CH_3Cl \rightarrow Cl^- + CH_3Fe$	100%	$0.16(3) - D_0$
1.3	0.7	$Fe^- + CH_3Br \rightarrow Br^- + CH_3Fe$	100%	$-0.15(4) - D_0$
1.9	1.0	$Fe^- + CH_3I \rightarrow I^- + CH_3Fe$	100%	$-0.45(3) - D_0$
<0.001	0	$Fe(CO)^- + CH_3F \rightarrow$ no reaction		$2.65(13) - D_1$
0.019[c]	0.01	$Fe(CO)^- + CH_3Cl \rightarrow Cl^- + CH_3Fe(CO)$	100%	$1.16(4) - D_1$
0.62	0.4	$Fe(CO)^- + CH_3Br \rightarrow Br^- + CH_3Fe(CO)$	100%	$0.86(5) - D_1$
1.2	0.9	$Fe(CO)^- + CH_3I \rightarrow I^- + CH_3Fe(CO)$	100%	$0.56(4) - D_1$
0.11[d]	0.06	$Fe(CO)_2^- + CH_3F \rightarrow CH_3Fe(CO)_2F^-$	50%	$2.72(16) - D_2$
		$\rightarrow CH_3FeF^- + 2CO$	40%	
		$\rightarrow$ other[e]	10%	
0.78[f]	0.4	$Fe(CO)_2^- + CH_3Cl \rightarrow Cl^- + CH_3Fe(CO)_2$	50%	$1.23(7) - D_2$
		$\rightarrow CH_3FeCl^- + 2CO$	35%	
		$\rightarrow Fe(CO)_2Cl^- + CH_3$	15%	
0.98	0.7	$Fe(CO)_2^- + CH_3Br \rightarrow Br^- + CH_3Fe(CO)_2$	50%	$0.92(8) - D_2$
		$\rightarrow CH_3FeBr^- + 2CO$	40%	
		$\rightarrow Fe(CO)_2Br^- + CH_3$	10%	
1.3	1.0	$Fe(CO)_2^- + CH_3I \rightarrow I^- + CH_3Fe(CO)_2$	60%	$0.62(7) - D_2$
		$\rightarrow CH_3FeI^- + 2CO$	30%	
		$\rightarrow Fe(CO)_2I^- + CH_3$	10%	
<0.001	0	$Fe(CO)_3^- + CH_3F \rightarrow$ no reaction		$3.41(21) - D_3$
0.22	0.1	$Fe(CO)_3^- + CH_3Cl \rightarrow Fe(CO)_3Cl^- + CH_3$	90%	$1.92(11) - D_3$
		$\rightarrow CH_3Fe(CO)Cl^- + 2CO$	10%	
0.56	0.4	$Fe(CO)_3^- + CH_3Br \rightarrow Fe(CO)_3Br^- + CH_3$	60%	$1.62(12) - D_3$
		$\rightarrow CH_3Fe(CO)Br^- + 2CO$	40%	
0.77	0.6	$Fe(CO)_3^- + CH_3I \rightarrow Fe(CO)_3I^- + CH_3$	60%	$1.31(12) - D_3$
		$\rightarrow CH_3Fe(CO)I^- + 2CO$	40%	
<0.001	0	$Fe(CO)_4^- + CH_3F \rightarrow$ no reaction		$3.90(42) - D_4$
<0.001	0	$Fe(CO)_4^- + CH_3Cl \rightarrow$ no reaction		$2.41(33) - D_4$
<0.001	0	$Fe(CO)_4^- + CH_3Br \rightarrow$ no reaction		$2.10(33) - D_4$
<0.001	0	$Fe(CO)_4^- + CH_3I \rightarrow$ no reaction		$1.80(33) - D_4$

[a] Reaction efficiency is the experimental rate constant divided by the calculated collision rate constant [36].

[b] For $E_{cm} = 0.3$ eV an additional ion product, $FeCl^-$ was observed.

[c] For suprathermal E_{cm}, this rate constant drops, then rises sharply; an additional ion product, $Fe(CO)Cl^-$ was observed at higher energies.

[d] The rate constant and product branching fractions were independent of buffer gas pressure in the range studied, 0.26–0.72 Torr.

[e] Several minor ion products were observed, notably 126 and 118 u (<10%), as well as 124, 128, and 131 u (<1%), and are suspected due to impurities in the CH_3F (98.5% pure, from PCR Products, Inc.).

[f] For suprathermal E_{cm} this rate constant drops considerably.

ple, in reactions of Fe^- with CH_3Br and CH_3I, the X^- product could be observed even if the neutral is $Fe + CH_3$—note that this will not change the conclusions drawn about any of the $Fe–CH_3$ bond strengths, however. Also included are reaction efficiencies, i.e. experimental rate constants divided by the collisional rate constants. The latter are calculated from classical trajectory theory for ion-polar molecule collisions [36], using dipole moments from [37] and polarizabilities from [38]. Table 1 also lists the reaction enthalpy for the production of X^- (whether or not X^- was an observed product); the enthalpies are determined from known methyl–halide bond strengths [39] and electron affinities of the halogen atoms [40] and $Fe(CO)_n$ [3,5–7]. The enthalpies are given in terms of the unknown iron–methyl bond energies at 298 K,

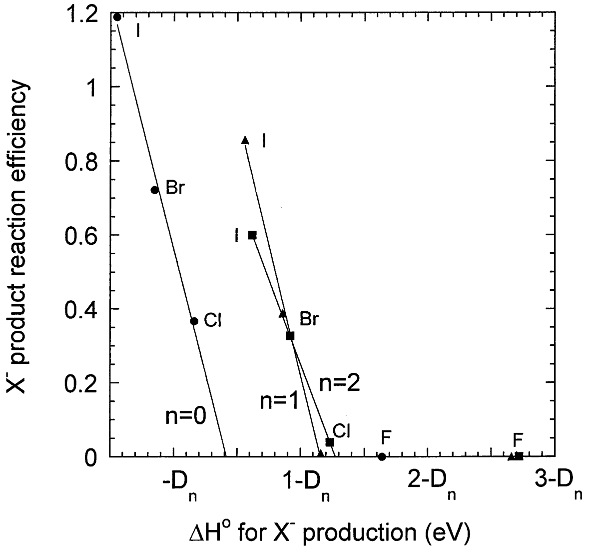

Fig. 1. Partial reaction efficiency of the X^- production channel for the reactions listed in Table 1, as a function of reaction enthalpy. This suggests that the reaction efficiency is directly dependent upon exothermicity, and hence a near-zero efficiency implies a thermoneutral reaction. From this principle the bond energies D_n may be deduced.

where D_n in the table denotes the $Fe(CO)_n$–CH_3 bond energy.

Our results are in good agreement with the limited data previously reported on $Fe(CO)_n^-$ reactions. McDonald et al. [10] studied the $Fe(CO)_3^- + CH_3Br$ reaction and measured a rate coefficient 29% greater than our result. They observed products $Fe(CO)_3Br^-$ (50%) and $CH_3Fe(CO)Br^-$ (50%), reasonably close to the product distribution we report. McElvany and Allison [14] saw only $Fe(CO)_2Cl^-$ from reaction of $Fe(CO)_3^-$ with CH_3Cl; they did not report the rate constant for the reaction. The nonreactivity of $Fe(CO)_4^-$ with the methyl halides is in agreement with the work of Jones et al. [12], McDonald et al. [13], and McElvany and Allison [14].

The simplest interpretation of the various reaction channels observed is that X^- formation occurs when the process is exothermic. Fig. 1 is a graph of reaction efficiency versus the reaction enthalpy for the X^- production channel for each of the reactions of Table 1. The total reaction efficiency is the measured rate constant divided by the calculated collisional rate constant. The reaction efficiency for X^- production is this ratio times the X^- branching efficiency. Fig. 1 shows the approximately linear correlation between the reaction efficiency and the reaction exothermicity for X^- production. The approximately linear increase in efficiency with reaction exothermicity is similar to the results obtained for slow halide transfer rates in CH_3X reactions with halide anions [41,42]. The main-group nucleophilic displacement reactions necessarily occur by X^- attack on the methyl carbon, producing a five-coordinate, high energy transition state. Theoretical models of this transition-state barrier have been developed which have been used to account for both the extremely slow X^- transfer rates and their increase with exothermicity [41,42]. Transition-metal anions have alternate pathways for the observed X^--forming reactions. By comparison to main-group anions, the metal fragments here have extremely small EAs, making reactions initiated by electron transfer a possibility. Indeed, the rate of reaction of Fe^- reacting with CH_3I is above “collisional” (although not so much as to be outside of the error limits of the experimental and calculated rates). Such a large rate can be indicative of electron transfer occurring at longer range than the orbiting impact parameter [43]. Electron transfer has been postulated as the initiating step in a number of $Fe(CO)_n^-$ reactions, for example, by Pan and Ridge [11]. Another possible reaction mechanism for all systems studied [except for reactions with $Fe(CO)_4^-$] is the oxidative addition of the methyl halide followed by elimination of X^-,

$$
\begin{aligned}
Fe(CO)_n^- + CH_3X &\rightarrow [(CO)_nFe(CH_3)X^-] \\
&\rightarrow (CO)_nFeCH_3 + X^- \qquad (2)
\end{aligned}
$$

The oxidative addition does not necessarily occur as a single, concerted addition—it might occur after initial electron transfer, a mechanism suggested by a number of researchers [1,14,15]. Oxidative addition intermediates, as well as products, for gas-phase reactions of $Fe(CO)_n^-$ have been postulated by others, for example, by McElvany and Allison [14,15], McDonald and co-workers [10,13,16–18], and by van den Berg et al. [24,25]. The structures of some products, for example,

$(CO)_2Fe(H)[C(CH_3)_3]^-$ [10] and $(CO)Fe(H)(OCH_3)^-$ [24] formed by reaction of $Fe(CO)_2^-$ with $HC(CH_3)_3$ and CH_3OH, respectively, have been confirmed by particularly nice isotopic data which support the oxidative addition products.

Oxidative addition/reductive elimination is a well-established mechanism for the catalysis of reactions such as hydrogenation, hydroformylation, or C–H activation by transition metal complexes in solution [44]. Experiments and calculational studies on metal complexes support the idea that oxidative addition of CH_3X to a metal center can occur with little activation energy [44]. Oxidative addition does depend on the electronic structure of the metal. The Fe^- has a d^7s^2 ground state [3], as does isoelectronic Co [45], but Ni^+ has a d^9 ground state [45], with the d^7s^2 at least 12 eV higher in energy [45] (the state has not been observed). The states with excitation to the p orbital may be more accessible for the Fe^- as well: in Co the first $d^7s^1p^1$ state is around 3 eV excitation [45]; again for Ni^+ the state is at least 12 eV about the ground state (the state has not been observed). The $d^7s^1p^1$ state of Fe^- would be expected to be at a smaller excitation energy than found in Co, by analogy to Ca^- and Sr^-, both of which have ground state s^2p^1 [46], whereas isoelectronic and Sc and Y have s^2d^1 ground states with the s^2p^1 states about 1.9 and 1.2 eV higher in excitation energy, respectively [45]. If the two sigma bonds to CH_3 and X are formed with *s–p* hybrid orbitals, for example, the lowering of the p orbitals could be important. The energetics and the electronic states of the $Fe(CO)_n^-$ clearly are a function of the number of CO ligands, as well [3].

For the series Fe^- through $Fe(CO)_3^-$, therefore, we suggest that there are reactive pathways, namely electron transfer and/or oxidative addition, whereby the X^- product can be formed where the transition-state barrier may be substantively reduced from that which might be incurred by "direct" nucleophilic attack on the methyl carbon. This does not imply that the oxidative addition is necessarily a barrierless process—in fact, the rate constants shown in Table 1 are less than collisional and they increase with exothermicity—observations which are consistent with kinetic models based on a transition-state barrier [41,42].

For $Fe(CO)_4^-$ the $EA[Fe(CO)_4] = 2.4 \pm 0.3$ eV makes electron transfer an energetically unlikely first step in CH_3X reactions; additionally, the 17-electron $Fe(CO)_4^-$ cannot undergo oxidative addition to form a 19-electron intermediate. Hence, $Fe(CO)_4^-$ can only react by "conventional" nucleophilic attack on the methyl carbon. Such direct reactions by 18-electron metal anions are notoriously slow. Even thermoneutral *proton* transfer reactions, e.g. between $(CO)_5Mn^-$ and $(CO)_5MnH$, take place in as little as 1 in 100 collisions [27,47,48]. The thermoneutral reaction

$$(CO)_5MnCH_3 + Br^- \rightarrow CH_3Br + (CO)_5Mn^-, \quad (3)$$

is not observed to proceed in either the forward or reverse direction (on the ion cyclotron resonance time scale, with a limit of about 1 in 100 collisions, or 10^{-11} cm^3 $molecules^{-1}$ s^{-1}), although the exothermic reactions of $(CO)_5MnCH_3$ with Cl^- and of $(CO)_5Mn^-$ with CH_3I are fast [49]. The rate limit of the SIFT instrumentation used here is about 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Finally, we note that $(CO)_4Fe^-$ does react with some neutrals, e.g. in the apparent proton transfer of reaction (1) [27], and in reactions with CF_3I and CF_3Br [13,34]. We postulate, based on the above experimental observations, that the nucleophilic reactions of $Fe(CO)_4^-$, if exothermic, would be observed under our experimental conditions.

When at least two CO ligands are present, ligand exchange is sometimes observed, where CH_3X replaces two CO ligands, presumably by its oxidative addition as CH_3 and X. This channel is seen as competitive with X^- formation, and indeed, the suggested oxidative addition intermediate shown in reaction (25) could be a common intermediate for both reaction channels. Halogen atom transfer may also occur competitively with either channel, and it becomes the dominant channel when X^- formation is endothermic. The only other reaction observed is an association channel seen with $Fe(CO)_2^- + CH_3F$. Finally, no reaction occurs if all reaction channels are endothermic, as is postulated for all reactions with $Fe(CO)_4^-$, and reactions of CH_3F with Fe^-, $Fe(CO)^-$, and $Fe(CO)_3^-$.

4. Iron–methyl bond energies

The assumption that the X^- reaction product is observed if its production is exothermic allows us to estimate the strength of methyl bonding to Fe and $Fe(CO)_n$. Consider the most straightforward case, for the iron–methyl bond energy in $Fe(CO)–CH_3$, or $D[Fe(CO)–CH_3]$. Our reasoning here is that the small reaction efficiency (1%) for X^- formation in the $Fe(CO)^- + CH_3Cl$ reaction suggests that this reaction is nearly thermoneutral, so that $D[Fe(CO)–CH_3]$ must be just strong enough to make the reaction proceed, albeit slowly. X^- formation proceeds rapidly for the $Fe(CO)^- + CH_3Br$ reaction, where there is an additional 0.3 eV energy; see Table 1 and Fig. 1. From the thermochemistry of the (presumed thermoneutral) reaction

$$Fe(CO)^- + CH_3Cl \rightarrow Cl^- + CH_3Fe(CO) \tag{4}$$

it can be shown that

$$D[Fe(CO)–CH_3] = D(CH_3Cl) - EA(Cl) + EA(Fe) \tag{5}$$

resulting in a value of $D[Fe(CO)–CH_3] = 1.2$ eV. We place an uncertainty of 0.2 eV on this value to account for the possibility that the observed slow reaction may be slightly endothermic, uncertainties in the thermochemical data (Table 1), and possible inaccuracies in measuring rate constants and product branching fractions.

Similarly, the reaction

$$Fe(CO)_2^- + CH_3Cl \rightarrow Cl^- + CH_3Fe(CO)_2 \tag{6}$$

appears to be nearly thermoneutral, with a partial reaction efficiency of 4%. Fig. 1 shows that the extrapolation of the efficiencies for the reactions with CH_3X ($X = Cl$, Br, I) to zero reaction efficiency, presumably the case near thermoneutrality, yields a value of $D[Fe(CO)_2–CH_3] = 1.3 \pm 0.3$ eV. A larger uncertainty is assigned in this case than for $D[Fe(CO)–CH_3]$ because there are competing reaction channels.

Likewise, the reactions

$$Fe^- + CH_3X \rightarrow X^- + CH_3Fe \tag{7}$$

were observed to take place for $X = Cl$, Br, I (Table 1). If lack of reaction is taken as a sign of endothermicity (and not activation energy), the data imply that the $Fe–CH_3$ bond strength lies between 0.13 eV (CH_3Cl reaction) and 1.76 eV (CH_3F nonreaction); the limits include the uncertainties of Table 1. The linear extrapolation of the reaction efficiency in Fig. 1 implies that $D[Fe–CH_3] \sim 0.4$ eV. Although there are no competing reaction channels in this case, the extrapolation to thermoneutrality for this case would hold only if the efficiency is linear with reaction exothermicity over a much larger range.

$Fe(CO)_{3,4}^-$ reactions with CH_3X do not yield any X^- products. Thus, only an upper bound may be placed on the respective iron–methyl bond energies. The results in Table 1 imply that $D[Fe(CO)_3–CH_3] <$ 1.4 eV and $D[Fe(CO)_4–CH_3] < 2.1$ eV. (These limits include the uncertainties on the energies listed in Table 1.) These conclusions for CH_3 bonding to $Fe(CO)_{3,4}$ obviously rely on the trends noted above, that X^- formation is exothermic, it will be observed. $Fe(CO)_4^-$ is too stable for any reaction with the CH_3X by any channel.

Only for $FeCH_3$ have estimates of the $Fe–CH_3$ bond energy been made, both experimentally and by quantum mechanical calculations. The current best experimental bond energy is determined from positive ion energetics by Armentrout and Kickel [50], $D^\circ_{298}[Fe–CH_3] = 1.46 \pm 0.30$ eV. This number is in good agreement with the best calculated value of Bauschlicher et al. of 1.45 eV (D°_0) [51]. These values are in keeping with periodic trends across the first transition series, i.e. the metal–methyl bond energy increases gradually from Mn to Cu [50,51]. We also note that the iron–hydride bond energy is somewhat better determined. Our value, from proton-transfer reactions to Fe^- is $D^\circ_{298}[Fe–H] = 1.52 \pm 0.19$ eV [32]. The work of Schultz and Armentrout [52] has converged to a similar value, $D^\circ_{298}[Fe–H] = 1.63 \pm 0.08$ eV. There is increasing evidence that the neutral bare metal atom–methyl bond energies are in the range of 0.2 eV smaller than that of the corresponding metal–hydrogen bond energies [50,53]. This suggests that the extrapolation of Fig. 1 for the Fe–CH_3 bond energy yields a value considerably (0.8–1.0 eV) too small, but that the Fe^- reactions with CH_3F and CH_3Cl do indeed provide a reliable upper (1.76 eV) and lower (0.13 eV) bounds to the Fe–CH_3 bond energy.

These data comprise the first set of data on iron–methyl bond energies for the CO–ligated complexes. There is some indirect evidence on the bond energy for $Fe(CO)_4CH_3$. We come back for comparison to the value of $D[(CO)_4Fe–H] \geq 2.60 \pm 0.52$ eV mentioned in Sec. 1 [27], where the large error limits are due to the large error limits on the gas-phase acidity of $(CO)_4FeH_2$ and EA[$Fe(CO)_4$]. For closed-shell metal complexes, methyl–metal bonds are generally ~0.5 eV weaker than the corresponding metal–hydrogen bonds [53]. This comparison suggests $D[Fe(CO)_4–CH_3] > 2.1 \pm 0.5$ eV, or applying the lower limit, that $D[Fe(CO)_4–CH_3] > 1.6$ eV. Comparing this value to our present upper bound to this bond energy, $D[Fe(CO)_4–CH_3] < 2.1$ eV, shows that the limits are consistent (including error limits), suggesting the bond energy is close to 2 eV. The values we determined in this work for the successively ligated iron–carbonyls are $D[Fe(CO)–CH_3] = 1.2$ eV $\pm$ 0.2 eV, $D[Fe(CO)_2–CH_3] = 1.3 \pm 0.3$ eV, $D[Fe(CO)_3–CH_3] < 1.4$ eV, and $D[Fe(CO)_4–CH_3] <$ 2.1 eV. We note that these values are all more consistent with the bond energies which might be expected by comparison to the literature value for $D^\circ_{298}[Fe–CH_3] = 1.46 \pm 0.30$ eV [50]. There appears to be little change in the bond energy for zero, one, two, and three CO ligands, but, if we include the lower limit for $D[Fe(CO)_4–CH_3]$ given above, there is an indication of a slight increase for four CO ligands.

5. Summary

Rate constants have been measured for atomic iron anions and successively ligated iron anions $Fe(CO)_n^-$ reacting with methyl halides. The results imply that X^- formation occurs as the dominant channel when exothermic. Ligand exchange, with CH_3 and X replacing two CO, and halogen atom transfer are also competitive reaction channels. $Fe(CO)_4^-$ does not react with the methyl halides.

Information on Fe–CH_3 bond strengths in $CH_3Fe(CO)_{0-4}$ is obtained from the results. The bond strengths are $0.13 \text{ eV} \leq D[Fe–CH_3] \leq 1.76$ eV, $D[Fe(CO)–CH_3] = 1.2 \pm 0.2$ eV, $D[Fe(CO)_2–CH_3] = 1.3 \pm 0.3$ eV, $D[Fe(CO)_3–CH_3] < 1.4$ eV, and $D[Fe(CO)_4–CH_3] < 2.1$ eV.

Finally, we note the following. (1) The very weak iron–methyl bond energies for each of these species is certainly one factor to consider in evaluating the particular small degree of reactivity of the anions with, e.g. CH_4. (2) By comparison to main-group anions, the metal fragments here have extremely small EAs, making reactions initiated by electron-transfer a possibility. Additionally, all except for 17-electron $Fe(CO)_4^-$ might react with the methyl halides by oxidative addition, thereby circumventing the five-coordinate methyl carbon intermediate needed for main-group nucleophilic reactions. This provides a second possible mechanism for the metal anions to undergo thermodynamically controlled rather than kinetically controlled reaction with the methyl halides.

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